

ACT LAUNCH Project No 299662



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Lowering Absorption process **UNcertainty, risks and **C**osts by predicting and controlling amine degradation**

Deliverable Nr. D4.3.1 & D5.2.5

Demonstration and assessment of mitigation technologies effectiveness on solvent degradation

Dissemination level		
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Executive summary

This deliverable is a combination from two LAUCH deliverables in the proposal: D4.3.1: Comparison of results and assessment of effectiveness of countermeasures and D5.2.5: Demonstration of mitigation technologies for an optimized solvent management'.

Solvent management is critical in CO₂ capture plants' operation, since solvent losses either in the form of emissions or in the form of degraded solvent can lead to operational issues, significant costs and, in extreme cases, failure to comply with permit regulations. These challenges can be avoided when suitable solvent management technologies are used. This work focuses on the investigation of solvent degradation management strategies, which were studied in the small-scale CO₂ capture plant LAUNCH rig#2 (25 kg CO₂/day) from TNO. The LAUNCH rig#2 is equipped with water washes on both absorber and stripper side, as well as a wash for quenching the inlet gas and bringing it to the desired temperature.

In this series of tests, two degradation control technologies were investigated in isolation in LAUNCH rig#2: the DORA technology and reclaiming. The tests were conducted at accelerated conditions based on the findings from the accelerated degradation protocol. More specifically, the tests were conducted at increased oxygen concentration (i.e. at 19.8 vol% O₂ in the flue gas, dry basis) since it was previously shown that higher oxygen concentration leads to higher formation rate of typical oxidative degradation products.

DORA, which stands for Dissolved Oxygen Removal Apparatus, was integrated in the LAUNCH rig#2, downstream of the absorber sump. Tests with 35 wt% MEA were first conducted, in which it was found that the oxygen concentration in the rich solvent, even without DORA, was close to the accuracy of the measuring sensor, which indicated that it would not be possible to measure the separation efficiency of DORA at these conditions. A new campaign with aged CESAR1 started, without DORA, to be used as a comparison basis. This test was stable and showed that the ammonia emissions of the solvent, while using a water wash, remained stable during 570 operating hours at around 3.5 mg/Nm³ despite the fact that the concentration of acids, which are typical oxidative degradation products, increased. In the beginning of the campaign with CESAR1 and DORA, the dissolved oxygen measurements with DORA in by-pass and with DORA in line indicated 76% oxygen removal. After a few hours of operation, problems arose with the water wash control leading to significant dilution incidents of the solvent. Due to these dilutions, it would be difficult to produce meaningful results with DORA, therefore it was decided to terminate the campaign.

The effect of reclaiming was studied by performing two 1-week long campaigns, one with degraded solvent and one with reclaimed solvent. The operation was similar in these two campaigns and stable without significant deviations along their duration. Slightly higher capture rates were seen during the campaign with the reclaimed solvent, which are most likely the result of having higher MEA content in the solvent (35 wt% MEA in the reclaimed solvent, compared to ~25 wt% MEA in the degraded one). The capture rate in the campaign with the degraded solvent dropped from 74% in the start to 63% in the end of the campaign, while with the reclaimed one, it remained the same, showing higher operating stability and predictability. Overall, the reclaimed solvent exhibited > 95% removal of acids, nitrates, and metals from the degraded solvent, in some cases even >99%. This means that these products were still detected in the start of the campaign with reclaimed solvent. It is seen that the rate of formation of formic and oxalic acid is similar in the two campaigns. Moreover, there is no clear effect in the behavior of metals in the system. Although the MEA content is not the same in the degraded and reclaimed solvent, these results provide a good indication regarding the differences in the degradation trends and metal accumulation between degraded MEA and reclaimed MEA.

Furthermore, when comparing the results between fresh MEA and the reclaimed solvent at similar conditions, we notice that the capture capacity is the same, and that ammonia emissions, the rate of formation of the degradation products and the rate of accumulation of metals is higher in the campaign with the reclaimed solvent than in the fresh solvent campaign. The reason for this might be the result of degradation products and metals being present already in the start of the campaign and along the campaign with the reclaimed solvent. The metals analyzed are Fe, Ni, Cr, Cu and Zn, the last two not being stainless steel constituents and most likely originating from a heating element in the plant. Ammonia emissions are higher in the reclaimed solvent campaign where water wash technology is also used, confirming the fact that water wash technology is not adequate for ammonia control.



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Page	3/23

The above observations, in combination with the observations made for CESAR1 within LAUNCH, where it was shown that the lowest increase rate of degradation products was for a mildly aged solvent without solvent management (instead of the clean solvent), warrant further investigations and demonstrate the uniqueness of each solvent in the choice of emission and solvent management control.



Table of Contents

1	INTRODUCTION	5
1.1	LAUNCH RIG #2	5
2	DEGRADATION CONTROL TECHNOLOGIES	7
2.1	DORA TECHNOLOGY	7
2.2	RECLAIMING	7
3	DORA TECHNOLOGY	10
3.1	OPERATIONAL SETTINGS.....	10
3.2	ANALYTICAL RESULTS.....	11
4	RECLAIMING	13
4.1	OPERATIONAL SETTINGS.....	13
4.2	ANALYTICAL RESULTS.....	14
4.3	COMPARISON RECLAIMED AND FRESH MEA.....	17
5	CONCLUSIONS AND SUGGESTED FUTURE WORK	21
6	REFERENCES	22
	APPENDIX	23
	APPENDIX A. DATA FROM LIQUID SAMPLE ANALYSIS BEFORE AND AFTER RECLAIMING.....	23



1 Introduction

Solvent management is critical in CO₂ capture plants' operation, since solvent losses either in the form of emissions or in the form of degraded solvent can lead to significant costs. These costs can be avoided when suitable technologies are used. This work focuses on the investigation of solvent degradation management strategies, which were studied in the small-scale CO₂ capture plant LAUNCH rig#2 (25 kg CO₂/day) from TNO. The LAUNCH rig#2 is equipped with water washes on both absorber and stripper side, as well as a wash for quenching the inlet gas and bringing it to the desired temperature.

In this series of tests, two degradation control technologies were investigated in isolation in LAUNCH rig#2: DORA technology and reclaiming. The tests were conducted at accelerated conditions based on the findings from the accelerated degradation protocol. More specifically, the tests were conducted at increased oxygen concentration (i.e. at 19.8 vol% O₂ in the flue gas, dry basis) since it was shown that higher oxygen concentration leads to higher degradation rate of typical oxidative degradation products (Deliverable D.1.3.1/D.4.2.1 Assessing the representativeness of accelerated degradation tests using the LAUNCH rigs and the DNM) Another possible degradation control strategy is activated carbon technology. This has been extensively studied within LAUNCH at RWE power plant in Niederaussem in terms of the effectivity of different types of active carbon filtering as a solvent management strategy, thus it was not included in this work. The results from the tests with activated carbon can be found in deliverable D5.2.2 (Moser et al., 2022).

Section 2 includes the description of the degradation control strategies studied, including operating principles of each technology. Sections 3 and 4 present the results of this work and discussion for the technologies' assessment; section 3 is dedicated to the DORA-related campaigns, while Section 4 is dedicated to the reclaiming-related campaigns. Section 5 summarizes the main findings of the work and recommends future work.

1.1 LAUNCH rig #2

TNO's LAUNCH rig#2 was used in order to investigate the efficiency of DORA technology. LAUNCH rig#2 is a CO₂ capture plant (5 Nm³/h flue gas capacity) which allows for 24/7 continuous operation. It enables tests of different solvents, multiple technologies for solvent management and process quality control under realistic conditions at TRL5. The rig can be operated with artificial or real flue gas, however this campaign was done with artificial flue gas in a composition similar to the ones of gas turbines. The gas inlet is controlled by mass flow controllers and an evaporator is connected to the lines to guarantee that the flue gas is saturated with water prior to entering the absorber column. Figure 1 depicts LAUNCH rig#2.



Figure 1: LAUNCH rig #2 at TNO

2 Degradation control technologies

Various strategies for solvent degradation mitigation have been proposed and studied in LAUNCH, from which DORA technology, reclaiming and activated carbon have been studied and demonstrated in this work.

2.1 DORA technology

DORA stands for Dissolved Oxygen Removal Apparatus, and it is a solvent-independent oxygen-selective membrane-based technology, developed by TNO, addressing oxidative degradation. By removing dissolved oxygen from CO₂ capture solvents, it aims to decrease the levels of oxidative degradation in the solvent and prolong solvent lifetime. The driving force for this removal can be provided either by a sweep gas in combination with vacuum or a liquid with an oxygen scavenger as shown in Figure 2. Details on the DORA technology and the membranes tested can be found in Deliverable report D.2.1.2 DORA: A Novel Technology for Lowering Solvent Degradation.

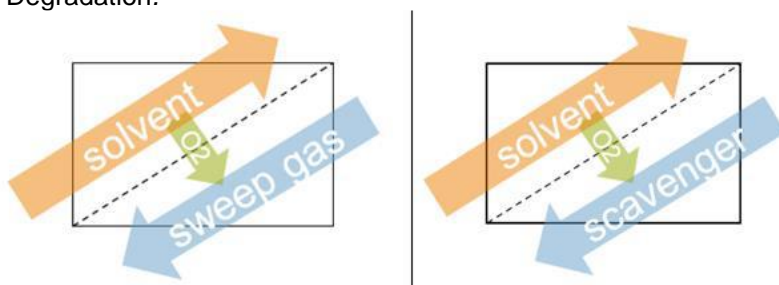


Figure 2: Working principle of DORA

TNO testing so far has included a commercially available porous membrane from 3M and a coated dense layer membrane developed by NTNU (V. Figueiredo et al., 2021). The porous membrane contactor was a Liqui-Cel® module packed with polypropylene hollow fibers with 25% porosity, effective pore size of 0.04 micron and corresponding inner and outer diameter of 200 and 300 micron, respectively. NTNU's dense layer membrane uses a porous polypropylene (PP) support (Celgard® 2400), thickness support of 25 µm and porosity of 41%. Due to the fact that the porous membrane showed pore wetting, the dense layer membrane by NTNU was prepared and planned to be used in a lab campaign, integrated in TNO's miniplant (Figure 3).



Figure 3: Dense layer membrane integrated in the miniplant

2.2 Reclaiming

Reclaiming is a solvent management technology aiming to purify the amine solvent by extracting, ideally pure, solvent constituents from the circulating inventory and is typically combined with alkali addition to release heat stable salts with acid gases other than CO₂ (i.e. NO₂ and SO_x). This is typically undertaken by 'thermal reclaiming', with the solvent being evaporated in one or more stages. The alternative is cleaning to remove impurities such as oxidative and thermal degradation products, including heat stable salts (HSS). Widely used cleaning methods are ion exchange and electrodialysis. Of course, reclaiming and cleaning can also be used



in combination, particularly if thermal reclaiming is unable to give good selectivity and unwanted impurities are unavoidably collected with the solvent.

In this work, thermal reclaiming is studied which has also been proposed as part of the Best Available Techniques (BAT) presented in the UKCCSRC 2022 report (Gibbins & Lucquiaud, 2022). Thermal reclaiming uses heat to evaporate the amine and separate it from degradation products with higher boiling point, metal ions and salts. Distillation is either performed in a small side stream, withdrawn from the solvent leaving the stripper reboiler so as to take advantage of its higher temperature, or it is performed off-site. Figure 4 shows the set-up used for the thermal reclaiming.

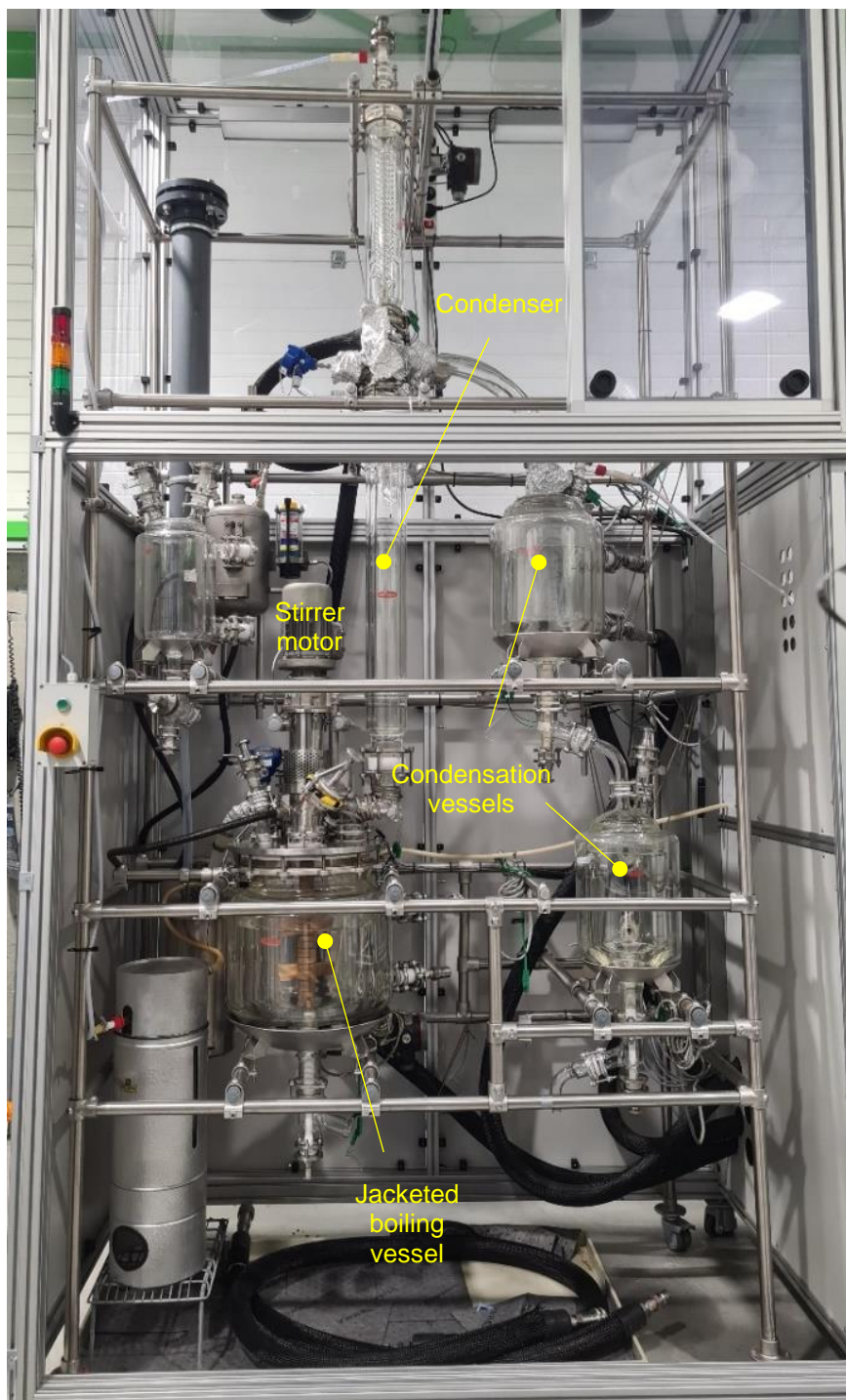


Figure 4: Reclaiming set-up

3 DORA technology

DORA was integrated in the rig, downstream the absorber sump. First, 35 wt% aqueous MEA and then degraded CESAR1 were used. The campaigns were not successful in demonstrating the DORA technology in the studied configuration, and the details are given in the sections below.

3.1 Operational settings

Experiments in WP1 of LAUNCH showed that oxygen depletion in aqueous MEA occurs at a significantly higher rate than CESAR1. Therefore, the campaign with MEA was designed to have as low residence time in the absorber sump as possible. When using flue gas with 5% vol% CO₂ (wet basis), lean solvent flowrate of 11.5 kg/h and 14 min residence time in the absorber sump, the oxygen concentration in the rich solvent, without DORA, was 0.02 mg/L. This is a very low value, close to the accuracy of the measuring sensor, which indicates that it would not be possible to measure the effect of DORA at these conditions. Modelling results with the Degradation Network Model, developed in LAUNCH, for 30 wt% MEA confirm this observation since they show that most of the degradation of the solvent, thus oxygen depletion, takes place in the packing of the absorber, and not in the sump. Therefore, when the solvent would reach DORA, the concentration would be already too small so as to have a meaningful effect on the degradation rate of the solvent. Deliverable report D1.3.4 is dedicated to the model description and the impact of DORA when it is used in alternative locations of the plant. The impact of DORA in the LAUNCH rig#2 was expected to be better measurable for solvents that are more chemically stable, therefore it was decided to terminate the MEA campaign (after approximately 70 operational hours) and continue the evaluation of DORA with CESAR1 instead.

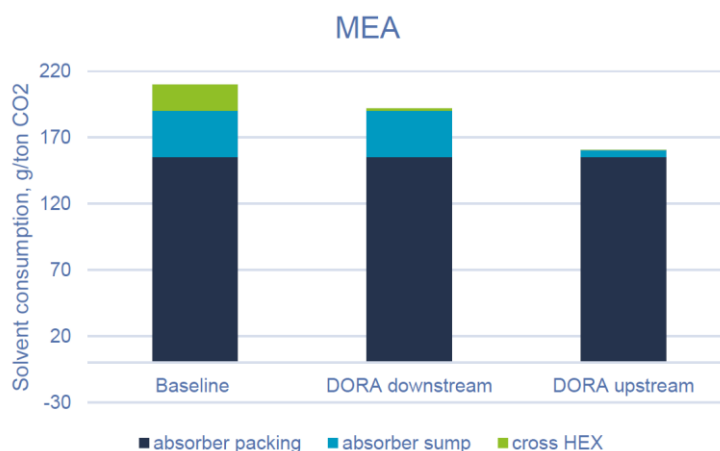


Figure 5: Modelling results regarding expected locations of occurring solvent degradation for 30wt% MEA, and effect of DORA location (Deliverable D1.3.4).

Aged CESAR1 solvent, which was delivered to TNO by RWE after 18.000 h of testing in their pilot plant, was used. First, a campaign without DORA was performed in order to evaluate the stability of the operation and the degree of degradation occurring in the solvent. The main operating parameters are presented in Table 1. This campaign reports 570 operating hours at stable conditions, with one incident of tripping due to level sensor failure. The average lean loading was 0.09 mol CO₂/mol amine and the rich loading was 0.30 mol CO₂/mol amine. Ammonia emissions were measured during the campaign and they stayed stable round 3.5 ppm.

Table 1- LAUNCH rig#2 operation parameters with aged CESAR1

Parameter	Unit	Representative value
Duration	hrs	570
Absorber		
N ₂ inlet flowrate	nL/h	3347
O ₂ inlet flowrate	nL/h	877
CO ₂ inlet flowrate	nL/h	247
H ₂ O inlet flowrate	g/h	236
Gas inlet composition, CO ₂	vol(%) wet	5.2
Gas inlet composition, O ₂	vol(%) wet	18.6
Gas inlet composition, H ₂ O	vol(%)	6.2
Lean solvent inlet flowrate	kg/h	11
L/G ratio	kg/kg	1.8
Temperature lean solvent inlet	°C	43.5
Liquid volume in absorber sump	L	1.7
NH ₃ emissions	mg/Nm ³	3.8
Stripper		
Gas flowrate out of the stripper	L/h	219
Pressure at stripper top	Barg	0.79
Temperature in reboiler liquid	°C	120.1
Liquid volume in reboiler	L	8.0
Cross Heat Exchanger		
Cold rich inlet temperature	°C	40.6
Cold lean outlet temperature	°C	42.5
Hot rich outlet temperature	°C	93.6
Hot lean inlet temperature	°C	107.6
Capture rate (%)		
Capture rate	%	81%

A campaign with CESAR1 and DORA started after the completion of the one without DORA. For this campaign, aged solvent with exactly the same starting point as the one in the campaign without DORA was used. The performance of DORA was assessed through the measurement of dissolved oxygen in the solvent. The dissolved oxygen in aged CESAR1 while DORA was by-passed was 0.47 mg/L (average of last 12 hours before DORA is inline) and when DORA was inline, it was 0.11 mg/L (average of first 12 hours with DORA). This demonstrates oxygen removal from the solvent thanks to DORA. Unfortunately, the effect of this removal technology's effect on the degradation trends of the solvent could not be further assessed because already in the beginning of this campaign (approximately 35 operating hours), problems arose with the water wash control leading to significant dilution incidents of the solvent. Due to these dilutions, it would be difficult to produce meaningful results with DORA, therefore it was decided to terminate the campaign.

3.2 Analytical results

Analytical results are available for the campaign with CESAR1 and without DORA. During this campaign, samples were taken in short intervals and sent for analysis (Ion Chromatography, IC, for amines, acids and nitrates, Karl-Fischer titration for water, and Inductively coupled plasma mass spectrometry, ICP-MS, for metals). Some variations in the water balance of the plant occurred, therefore the results in this section are shown water-corrected based on the 60.3 wt% H₂O in the original formulation of CESAR1. The results correspond to lean liquid samples.

The formation of the oxidative degradation products measured in this work, i.e. acetic, formic, lactic, oxalic, propionic, pyruvic, along the campaign is shown in Figure 6. After 570 hours, acetic, formic and oxalic acid, increased from 1256, 1729 and 376 mg/kg to 1512, 1786 and 460 mg/kg, respectively.

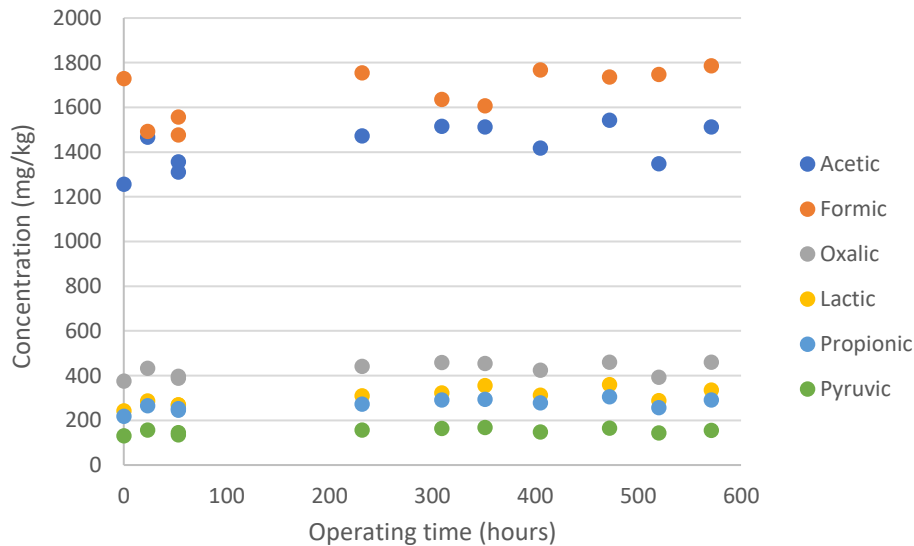


Figure 6: Acids' concentration progression during the CESAR1 campaign.

Figure 7 shows the concentration of Fe, Cr, Ni, Cu and Zn along the campaign. A small increase is shown in the start of the campaign for all metals. The concentration of Fe, Ni and Cr seems to stabilize around 2, 5 and 2 mg/kg respectively. Interestingly, the concentration of Cu increased from almost zero to 2 and seems to stabilize around this value, while the concentration of zinc kept increasing during the campaign starting from almost 0 and reaching approximately 5 mg/kg. Fe, Ni and Cr are constituents of stainless steel and, thus, their presence can be expected, however Cu and Zn are not found in this material and most likely these "foreign" metals originate from a heating element in the LAUNCH rig#2.

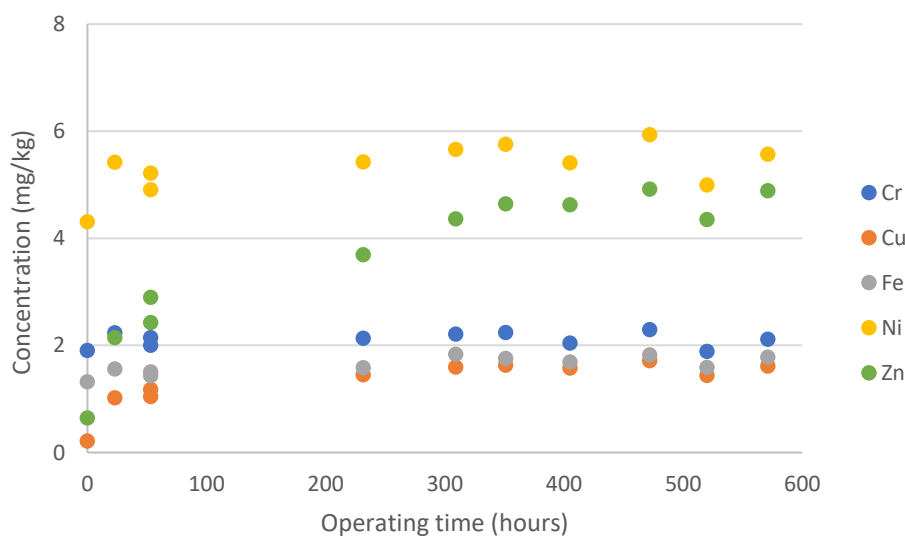


Figure 7: Metals' concentration progression during the CESAR1 campaign.

4 Reclaiming

The effect of thermal reclaiming was studied by performing a 1-week long campaign (Campaign Rec1) with degraded MEA solvent, then reclaiming the entire solvent inventory, and afterwards operating the miniplant for another 1-week long campaign with the reclaimed solvent (Campaign Rec2). Synthetic flue gas was used. The aged solvent was provided by AVR in early 2022. The results in terms of miniplant operational parameters and solvent degradation are shown in this section.

4.1 Operational settings

Campaign Rec1 with degraded MEA was stable and lasted 166 operating hours. After this, the solvent was reclaimed. Thermal reclaiming was used, by adding 3M NaOH and using 130°C temperature and reduced pressure down to 910 mbara. The amount added was based on the amount of acids quantified in the solvent, and a 1.5 factor overestimation to ensure NaOH was in excess. The recovery rate of MEA in the reclaimed solvent was 30%, therefore an optimized procedure for MEA reclaiming is needed. Upon reclaiming, fresh aqueous MEA was added to the reclaimed amount in order to reach 35 wt% aqueous MEA. Of the total MEA in the solvent, 78% was fresh MEA. As it is explained later, the MEA concentration was lower in Campaign Rec1 than expected, thus a higher amount of fresh MEA was added to reach the 35 wt%. The reclaimed solvent was used for another 168 operating hours (Campaign Rec2) in order to compare its removal capacity with the one with degraded solvent, as well as follow the degradation behavior of aged and reclaimed MEA.

The operation parameters recorded in the start and in the end of the two campaigns are presented in Table 2. It can be seen that, for both campaigns, the operation was quite stable without significant deviations along the duration of each campaign.

Table 2- LAUNCH rig#2 operation parameters

Parameter	Unit	Campaign Rec1		Campaign Rec2	
Duration	hrs	166		168	
		Start	End	Start	End
Absorber					
N ₂ inlet flowrate	nL/h	3347	3347	3319	3347
O ₂ inlet flowrate	nL/h	877	877	877	877
CO ₂ inlet flowrate	nL/h	247	247	247	247
H ₂ O inlet flowrate	g/h	220	238	220	210
Gas inlet composition, CO ₂	vol(%) wet	5.2	5.2	5.2	5.2
Gas inlet composition, O ₂	vol(%) wet	18.5	18.4	18.6	18.5
Gas inlet composition, H ₂ O	vol(%)	5.8	6.2	5.8	5.5
Lean solvent inlet flowrate	kg/h	11.3	11.5	11.2	11.3
L/G ratio	kg/kg	1.8	1.9	1.8	1.8
Temperature lean solvent inlet	°C	38.7	38.3	39.1	38.8
Temperature Gas inlet	°C	36.4	36.3	35.9	36.0
Lowest packing ((bottom – 4.30 m)	°C	43.1	42.6	45.4	44.8
Intermediate packing (low – 2.40 m)	°C	54.0	51.9	61.5	60.6
Intermediate packing (high – 0.48 m)	°C	55.6	53.6	60.6	59.8
Absorber gas outlet	°C	44.5	42.6	45.6	44.4
Liquid volume in absorber sump	L	1.3	0.9	1.0	0.7
MEA emissions	mg/Nm ³	5.4	6.3	1.4	0.01
NH ₃ emissions	mg/Nm ³	79.7	101.0	43.8	50.1
Stripper					
Pressure in stripper top	Barg	0.79	0.78	0.79	0.79

stripper T (top – 1,11 m packing depth)	°C	71.10	70.16	75.53	74.89
stripper T (1.96 m packing depth)	°C	87.88	88.36	89.08	89.41
stripper T (2.81 m packing depth)	°C	92.27	88.55	94.38	93.28
stripper T (3.66 m packing depth)	°C	99.82	95.09	101.35	100.17
stripper T (bottom – 4.25 m)	°C	108.20	105.66	109.96	109.34
Temperature in reboiler liquid	°C	120.2	120.2	120.1	120.1
Liquid volume in reboiler	L	8.0	8.1	8.0	8.0
Cross heat exchanger					
Cold rich inlet temperature	°C	38.8	38.3	38.4	38.8
Cold lean outlet temperature	°C	40.4	40.1	40.1	40.5
Hot rich outlet temperature	°C	93.9	94.9	94.9	93.6
Hot lean inlet temperature	°C	107.5	108.5	107.3	107.3
Capture rate					
Capture rate	%	74%	63%	79%	79%

It is observed that the L/G ratio and the inlet gas flowrate and composition are the same for both campaigns. In addition, the volume in absorber sump and reboiler were kept very similar in both campaigns, thus the residence times, which affect the degradation profiles, are also similar. Higher capture rate is achieved with the reclaimed MEA (calculated from CO₂ produced), 79% compared to 63-74% seen with the degraded solvent. The reason for this is believed to be the higher MEA concentration in the reclaimed solvent compared to the one in the degraded solvent, as explained in the next sub-section 4.2. One can also see that the capture rate in Campaign Rec1 decreased from 74% in the start to 63% in the end of the campaign, while in Rec2 remained the same. The lean loadings in Rec1 and Rec2 were 0.23 and 0.28 mol CO₂/mol amine in average, respectively for the two campaigns. Rich loadings are not reported, since the measurement was performed by ATR-FTIR methodology and it was later found that this method is not sufficiently accurate to monitor the composition of degraded solvent (see sub-section 4.2 for details). The temperature profiles of both absorber and stripper are consistently higher in Campaign Rec2 than Campaign Rec1, which is in line with the higher capture rate and, thus increased CO₂ uptake. Moreover, amine and ammonia emissions measured at the top of the absorber indicate reduction of 77% and 56% for MEA and NH₃, respectively, after the solvent was reclaimed.

4.2 Analytical results

In both campaigns, the solvent composition was monitored by conducting ATR-FTIR measurements on a daily basis for MEA, water, CO₂ in lean and rich samples and it was controlled to be 35 wt% MEA. In the end of each campaign, selected number of samples were analyzed by IC for the amines, acids and nitrates, by Karl-Fischer titration for water, and by ICP-MS for metals. In this section, the concentration values are presented as measured and can be found in the Appendix A.

Overall, the reclaimed solvent exhibited > 95% removal of acids, nitrates, and metals compared to the degraded solvent, in some cases even > 99%.

The IC results for Campaign Rec1 showed that the MEA content was ~26 wt%, instead of 35 wt%. The total amount of the components included in the analysis summed up to 800 g/kg, indicating that 20 wt% of the sample is undefined material (based on the components chosen to be analyzed). This is not uncommon for degraded solvents. Morken et al. reported undefined components up to 8 wt% of the total mass during a solvent management study with MEA at TCM (Morken et al., 2019). Further, results from AVR, where the solvent was taken from, have been published showing that the plant had indeed been operated at approximately 25 wt% MEA (Ros et al., 2022). This indicates that the ATR-FTIR methodology used (calibration curves made with fresh solvent) is not sufficiently accurate to monitor the composition of degraded solvent.

During Campaign Rec1, the degradation products acetic, formic and oxalic acid started from the concentration of 887, 6039 and 2073, respectively, and reached 1217, 6324 and 2305 mg/kg in the end of the campaign.

These correspond to 37%, 5% and 11% increases (relative). Comparing with the results of Rec2, two observations can be made. Firstly, the concentration of the acids has significantly decreased, as expected; acetic acid was not identified in the analysis along the full campaign Rec2, and formic and oxalic acid measured at the levels of 259 and 18 mg/kg, respectively. Secondly, the rate of formation of these substances is similar in the two campaigns. This is illustrated in the slope of the fitting equations to the data in Figure 8 and Figure 9 (linear fitting in the case of formic acid in Rec1 does not completely represent the trend, however it gives a good indication of the behavior). Due to the large difference in the values in the two campaigns, the left and the right y-axis are assigned to the degraded solvent and the reclaimed solvent, respectively, making it possible for the reader to see the trends. In addition, nitrate increases slightly faster for the degraded solvent than in the reclaimed one, while no nitrite is identified in the degraded solvent.

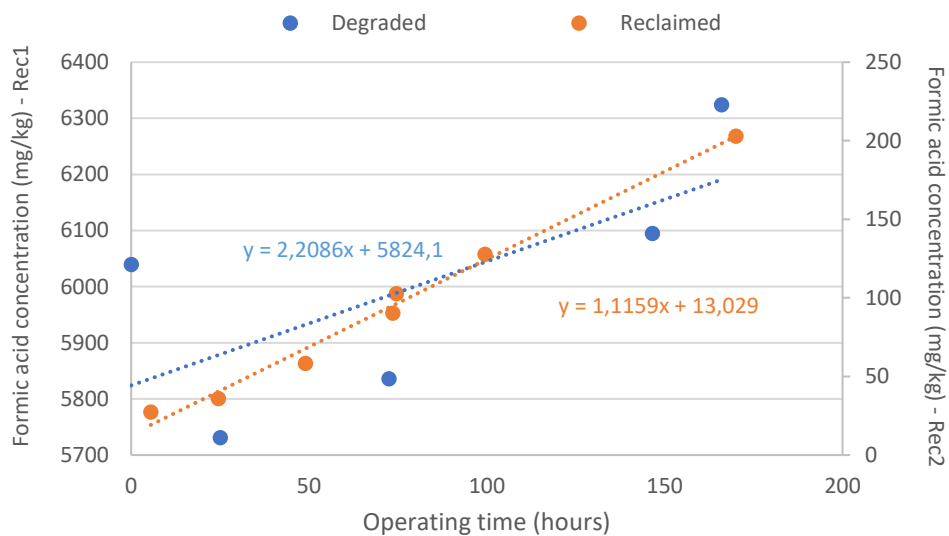


Figure 8: Formic acid concentration progression for the degraded solvent (Campaign Rec1) and the reclaimed solvent (Campaign Rec2).

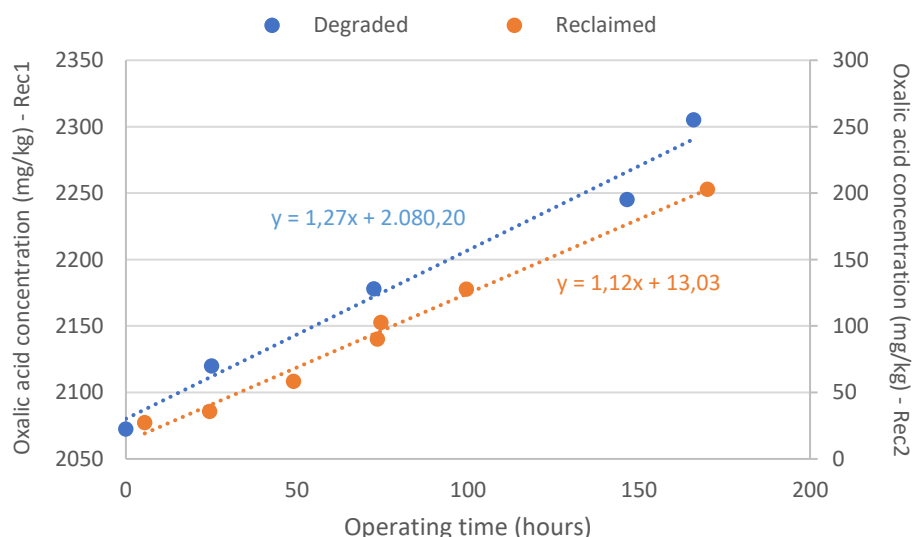


Figure 9: Oxalic acid concentration progression for the degraded solvent (Campaign Rec1) and the reclaimed solvent (Campaign Rec2).

As far as metals are concerned, there is no clear trend in the accumulation of these components in the solvent systems. The slope in the case of nickel is similar between the two campaigns, then the slope for iron and chromium is sharper for the degraded solvent than in the reclaimed one (Fe, Figure 10), and the opposite is

seen for copper and zinc (Zn, Figure 11). The higher rate of copper and zinc accumulation is attributed to failure of a heating element of the rig, as also seen in the campaign with CESAR1 during the DORA testing work (sub-section 3.2).

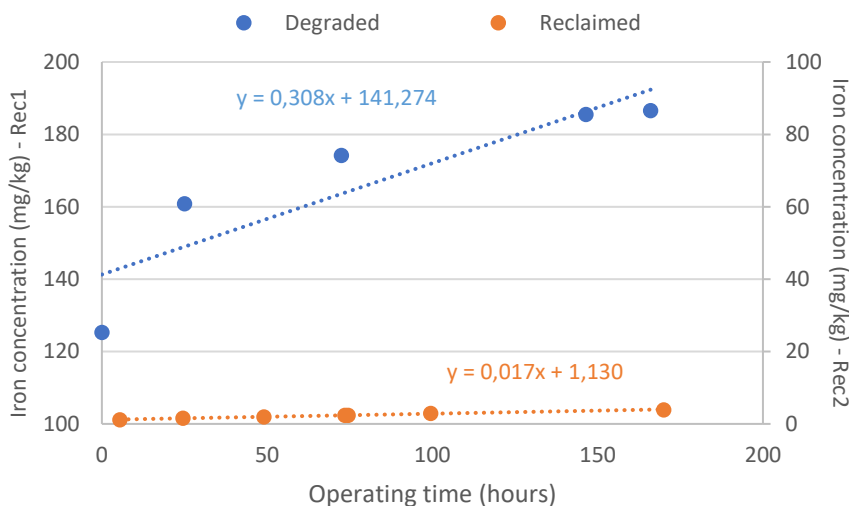


Figure 10: Iron concentration progression for the degraded solvent (Campaign Rec1) and the reclaimed solvent (Campaign Rec2).

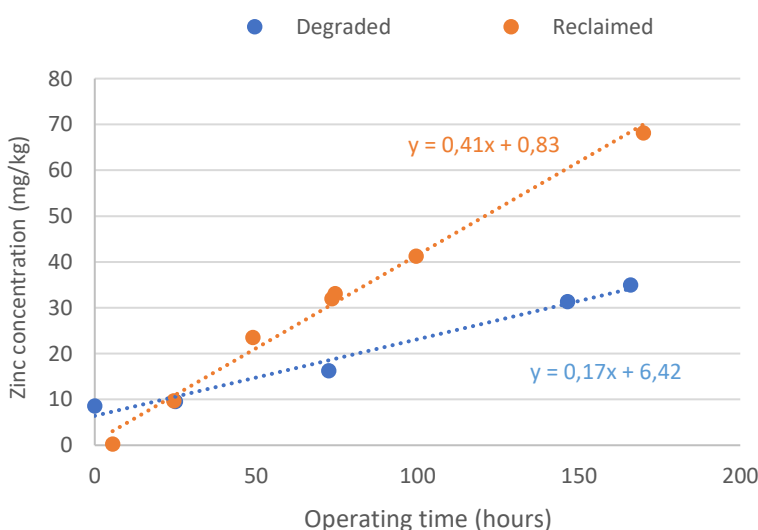


Figure 11: Zinc concentration progression for the degraded solvent (Campaign Rec1) and the reclaimed solvent (Campaign Rec2).

Within LAUNCH, one of the learnings from the activities with CESAR1, and specifically, the application of ion exchange as a degradation control strategy, is that the lowest increase rate of degradation products is not found for the fresh clean solvent, but for mildly aged solvent without solvent management (Moser et al., 2022). In this work with MEA, we see that the rate is rather similar for the oxidative degradation products (formic and oxalic acid) between the degraded and the reclaimed solvent, while different metals show different behavior in the two campaigns. It is reminded that the reclaimed solvent is partially fresh, as explained earlier, in order to reach the 35 wt% MEA. Although the amine content was not the same in the degraded and reclaimed solvent, these results provide a good indication regarding the effect of reclaiming in the degradation rate and metal accumulation between degraded MEA and reclaimed MEA.

4.3 Comparison reclaimed and fresh MEA

It is interesting to see how a system of fresh MEA compares with a system of a reclaimed one. For this reason, we compared the results from Campaign Rec2 with previous campaigns which were performed during the study of accelerated degradation strategies with fresh MEA as a starting point. Specifically, the campaign with the same gas composition as in this work, similar MEA concentration in the solvent, i.e. 37 wt% MEA, and stripper temperature of 120 °C was used (see details on LAUNCH Deliverable D.1.3.1/D.4.2.1 Assessing the representativeness of accelerated degradation tests using the LAUNCH rigs and the DNM).

The L/G ratio used in the fresh MEA campaign was 1.9 kg/kg and in the reclaimed solvent one it was 1.8 kg/kg. The pressure in the stripper was 810 barg for fresh MEA and 790 barg for reclaimed MEA, while the temperature profile in the absorber was similar, with the bulge in the absorber occurring in the intermediate part of the column and reaching 61-62°C. The loadings between the two systems are similar: lean=0.27 and rich=0.44 mol/mol for fresh solvent, while for the reclaimed solvent the loadings are for lean=0.29 and rich=0.46 mol/mol. Therefore, the cyclic capacity is the same, i.e. 0.17 mol/mol.

The comparison in terms of emissions is not straight forward because in the fresh MEA campaign, no water washes were present. In-line with this, the MEA emissions were higher in the fresh MEA campaign with ~100 mg/Nm³ while emissions down to ~1mg/Nm³ seen in the Rec2 campaign. Ammonia emissions are higher in the Rec2 campaign with the water wash presence, with emissions ~50 mg/Nm³ while in the fresh MEA campaign ~10 mg/Nm³ NH₃ were seen, confirming the fact that water wash technology is not adequate for ammonia control.

In the analytical front, it is seen that the rate of formation for oxidative degradation products, i.e. acids, but also accumulation of metals is higher in the reclaimed solvent than in the fresh one. The starting concentration is always higher for the reclaimed solvent and this may be the reason of these trends. For example, the comparison for oxalic acid is illustrated in Figure 12. The concentration for the reclaimed solvent at 5.5 operating hours is 27.4 mg/kg while the one for fresh solvent is 1.6 mg/kg after 24 operating hours. In the fresh solvent, the concentration of oxalic acid is 5.2 mg/kg after 144 operating hours, and 202 mg/kg after 170 operating hours in the reclaimed solvent. No data are available after exactly the same operating hours, therefore the comparison is attempted between the final point of the Rec2 campaign, and the data point in the fresh solvent campaign obtained at the closest operating hours.

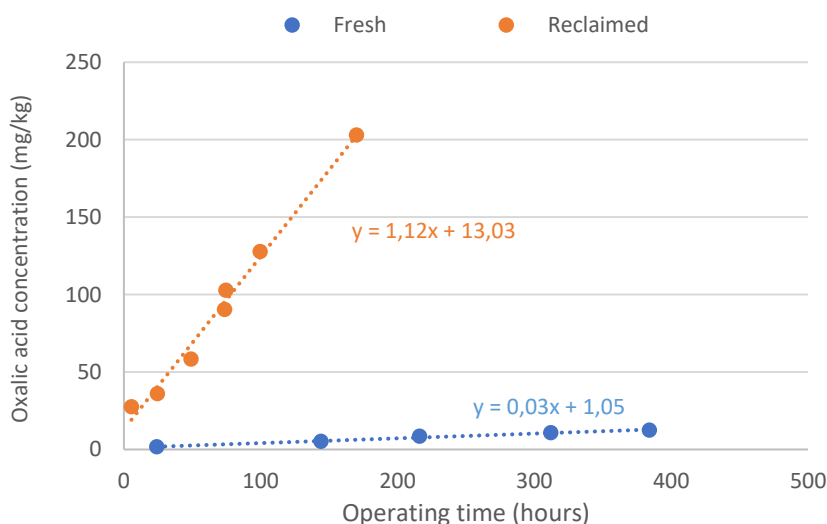


Figure 12: Oxalic acid concentration progression for fresh 30wt% MEA solution and the reclaimed solvent in this work (Campaign Rec2).

The solvent was neutralized with NaOH prior to reclaiming, therefore no acids would be expected to be present. These higher starting concentrations of degradation products might also be the reason for the

increased ammonia emissions seen after the water wash in the reclaimed solvent compared to the fresh one. Observing the presence of acids after 5.5 hours can be the result of either liquid entrainment during reclaiming, fast degradation within the first hours or remnant solvent amounts in the LAUNCH rig#2 from campaign Rec1. Regarding the fast degradation scenario, it should be possible to fit the trend line through zero point in order to follow the behavior of the rest of the points, however this is not the case. Moreover, the LAUNCH rig#2 was cleaned twice with demineralized water between Rec1 and Rec2, though it is possible that traces had remained in the rig.

As far as the presence of metals is concerned, the same observations of higher metal accumulation rate in the reclaimed solvent compared to the fresh one are made for all metals analyzed (Cr, Cu, Ni, Fe, Zn). The results for Fe as well as the “foreign” Zn (which is not a typical stainless steel component) are shown in Figure 13 and Figure 14. Although the starting concentration of iron in the fresh solvent is not zero, due to a non-operating time between the loading of the solvent and the start of the campaigns, the rate of accumulation is much lower than in the reclaimed solvent. In the case of zinc, the starting concentration in the reclaimed solvent is 0.3 mg/kg after 5.5 operating hours while the one for fresh solvent is 1.5 mg/kg after 24 operating hours. Its concentration in the reclaimed solvent increases very sharply reaching 68 mg/kg after 170 hours, while for the fresh solvent reaches 1.5 mg/kg after 144 operating hours.

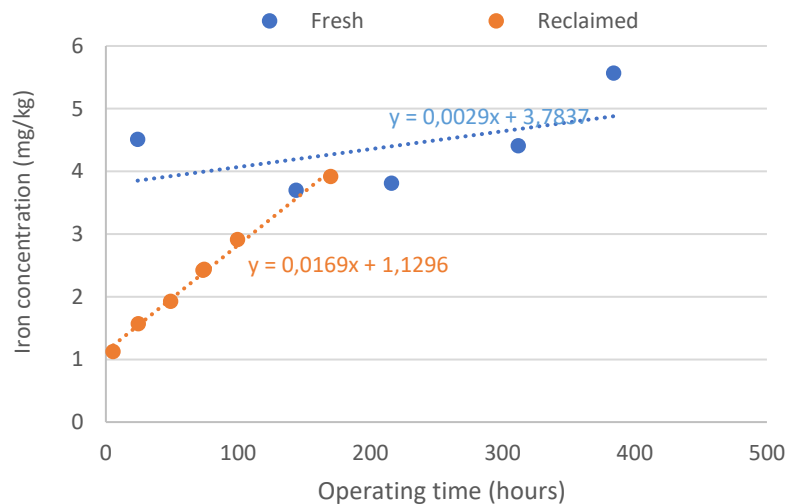


Figure 13: Iron concentration progression for fresh 30wt% MEA solution and the reclaimed solvent in this work (Campaign Rec2). It is noted that the non-zero starting concentration in the fresh solvent is a result of non-operating time between loading the solvent and the start of the campaign.

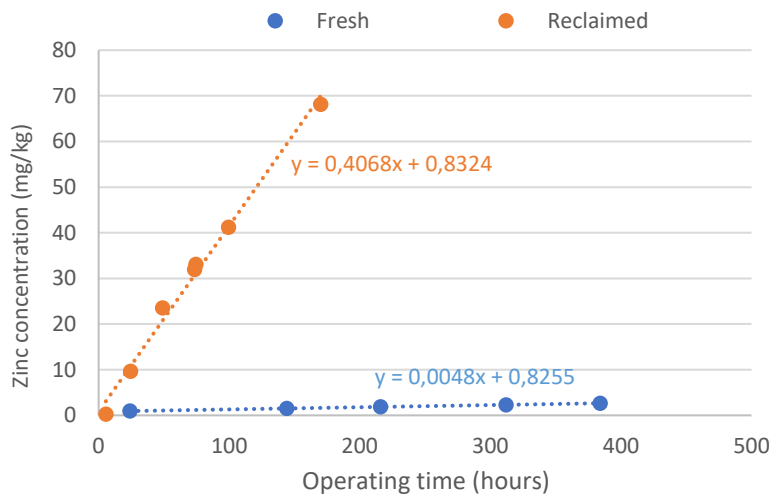


Figure 14: Zinc concentration progression for fresh 30wt% MEA solution and the reclaimed solvent in this work (Campaign Rec2).

In order to investigate the role of zinc presence in the campaign, the concentration of Fe and Zn with operating hours in the LAUNCH rig#2 during the last 2 years of the project are shown in Figure 15 Figure 16 (See LAUNCH Deliverables D4.1.1 and D1.3.1/D4.21). It is noted that zinc was not analyzed in the campaign with CESAR1 during the operating hours between 2500 and 4000 h, thus no data are available, and that the CESAR1 and MEA - Rec1 campaigns were performed with aged solvents already containing metals. The most interesting part of this graph for this discussion is the last part during the operating hours after the 4000 operating hours. These correspond to 3 consecutive campaigns, the testing with CESAR1 during the DORA-related work, and the reclaiming Rec1 and Rec2 campaigns.

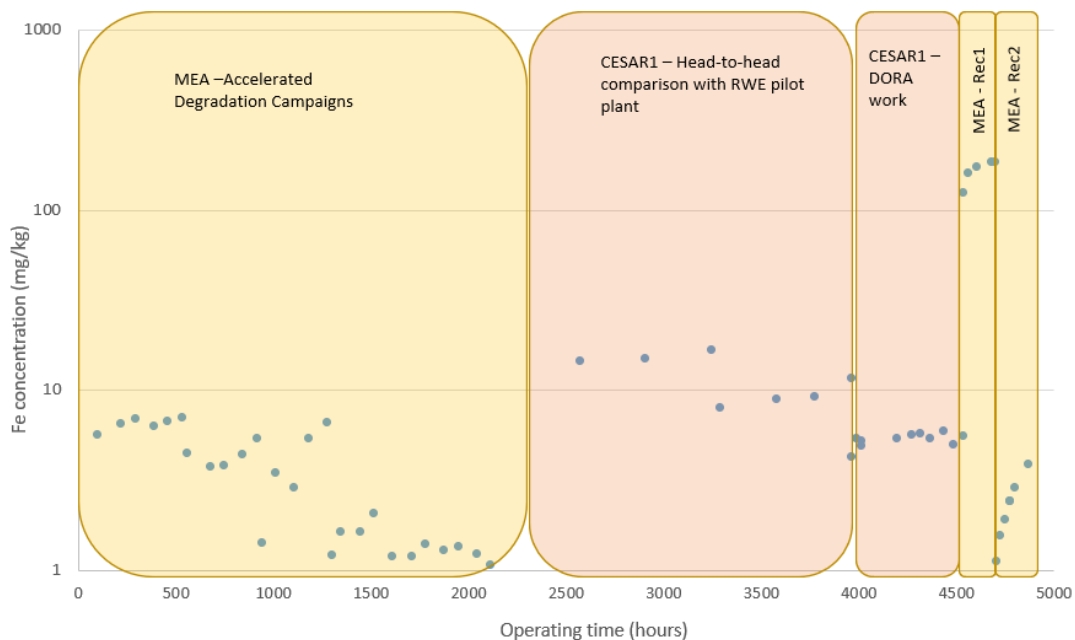


Figure 15: Iron concentration as a function of operating hours during the demonstration campaigns of LAUNCH.

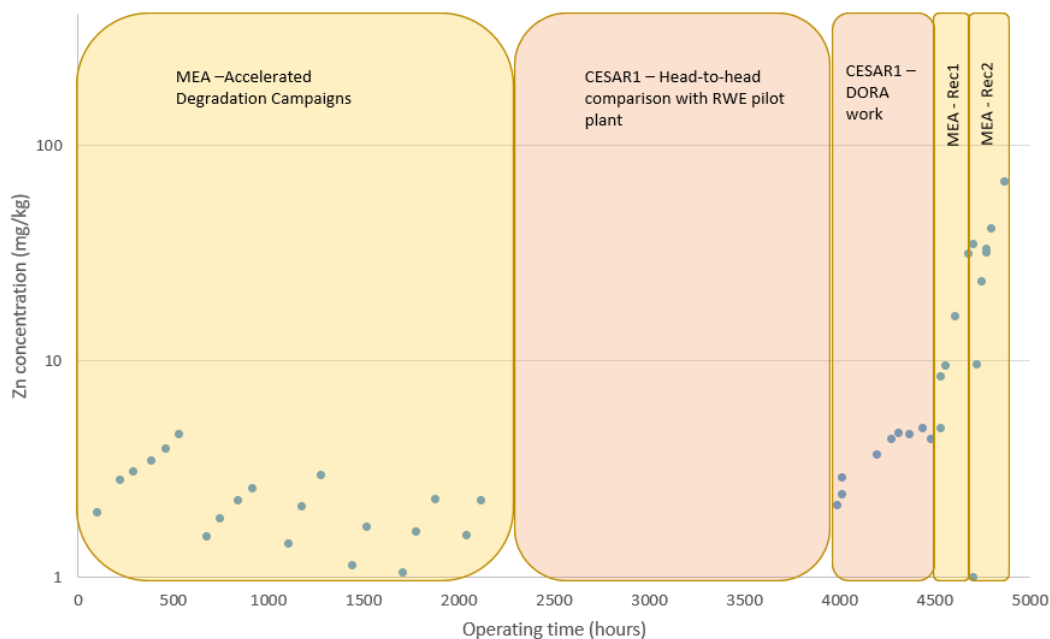


Figure 16: Zinc concentration as a function of operating hours during the demonstration campaigns of LAUNCH.

It can be seen that the slope during 4000 to 4500 operating hours is lower than the slope in Rec1 and Rec2, due to different conditions and solvent, with the end value being similar to the ones seen during the initial accelerated degradation campaigns. The same trend is followed for zinc up to the campaign until 4500 operating hours, with the value of zinc not exceeding 5 mg/kg. However, in Campaign Rec1 and Rec 2, the rate is much higher than the rates seen before, although in the case of Rec2 the starting concentration was 0.27 mg/kg which is similar to the initial MEA campaigns. Therefore, there are definitely some undergoing phenomena in the reclaimed solvent, due to the solvent's complex degradation products matrix and/or catalytic degradation reactions in the presence of metals, leading to higher oxidative degradation products formation rates. It is also possible that the exposed surface releasing the Zn and Cu into the solvent is changing over time, with more surface progressively exposed due to corrosion, perhaps with pitting and brass dezincification. That Cu was not observed to increase significantly in the earlier runs but did so in the final tests is evidence that something has changed at the likely common source (a heating element) for both of these metals. Note, however, that alloys containing Cu or Zn would not normally be exposed anywhere in the wetted path on commercial MEA plants.

Last but not least, it is interesting to notice in both Figures Figure 12 and Figure 13, that the data for the fresh solvent extend to approximately 380 operating hours. In this period, no exponential behavior is seen for fresh MEA and the concentrations remain much lower than the ones in the reclaimed solvent.

5 Conclusions and Suggested future work

Two degradation control technologies were investigated in isolation in LAUNCH rig#2, i.e. DORA technology and reclaiming. The tests were conducted at accelerated conditions based on the findings from the accelerated degradation protocol. More specifically, the tests were conducted at increased oxygen concentration (i.e. at 19.8 vol% O₂ in the flue gas, dry basis) since it was shown that higher oxygen concentration leads to higher degradation rate of typical oxidative degradation products.

In order to assess the effect of DORA, a campaign needs first to be performed without DORA to be used as a baseline. When MEA solvent was used for this in the LAUNCH rig#2, it was found that the oxygen concentration in the rich solvent, without DORA, was too low and close to the accuracy of the measuring sensor, which indicates that it would not be possible to measure the effect of DORA at these conditions. Based on modelling results with the Degradation Network Model, developed in LAUNCH, for 30 wt% MEA, most of the degradation of the solvent takes place in the packing of the absorber, and not in the sump. Therefore, for future testing with MEA it is recommended to use either lower residence time in the absorber (<14 min) and/or integrate DORA upstream the sump.

Tests with degraded CESAR1 and without DORA were stable and showed that the ammonia emissions of the solvent, while using a water wash, remained stable during 570 operating hours at around 3.5 mg/Nm³ despite the fact that the concentration of acids, which are typical oxidative degradation products, increased. Dissolved oxygen measurements with DORA by-passed and with DORA inline indicated 76% oxygen removal. Unfortunately, already in the beginning of the campaign with CESAR1 and DORA, problems arose with the water wash control leading to significant dilution incidents of the solvent. Due to these dilutions, it would be difficult to produce meaningful results with DORA, therefore it was decided to terminate the campaign.

The effect of reclaiming was studied by performing two 1-week long campaigns, one with degraded solvent and one with reclaimed solvent. The operation was similar in these two campaigns and stable without significant deviations along their duration. Slightly higher capture rates were seen during the campaign with the reclaimed solvent, which are most likely the result of having higher MEA content in the solvent (35 wt% MEA in the reclaimed solvent, compared to ~25 wt% MEA in the degraded one). The capture rate in the campaign with the degraded solvent dropped from 74% in the start to 63% in the end of the campaign, while with the reclaimed one, it remained the same, showing higher operating stability and predictability. Overall, the reclaimed solvent exhibited > 95% removal of acids, nitrates, and metals from the degraded solvent, in some cases even >99%. This means that these products were still detected in the start of the campaign with reclaimed solvent. It is seen that the rate of formation of formic and oxalic acid is similar in the two campaigns. Moreover, there is no clear effect in the behavior of metals in the system. Although the MEA content is not the same in the degraded and reclaimed solvent, these results provide a good indication regarding the differences in the degradation trends and metal accumulation between degraded MEA and reclaimed MEA.

When comparing the results between fresh MEA and reclaimed MEA solvent, we notice that although the capture capacity is the same, more ammonia emissions are present when using the reclaimed solvent. Further, the rate of formation of the degradation products and the metals accumulation is always higher in the reclaimed solvent than the fresh one, which might be the result of degradation products and metals being present already in the start of the campaign with the reclaimed solvent. Ammonia emissions are higher in the reclaimed solvent campaign where water wash technology is also used, confirming the fact that water wash technology is not adequate for ammonia control.

The above observations, in combination with the observations made for CESAR1 within LAUNCH, where it was shown that the lowest increase rate of degradation products was for a mildly aged solvent without solvent management (instead of the clean solvent) warrant further investigations. Longer campaign with reclaimed MEA would be beneficial for identifying if there is a point after which the degradation rate is minimized, like in CESAR1, and what the role of metals such as the atypical amounts of Cu and Zn was. The need of reclaiming in combination with a metal-removing technology, such as ion-exchange, should also be evaluated. Last but not least, developing reclaiming and cleaning procedures for solvent blends, such as CESAR1, would be beneficial for the implementation and acceleration of CO₂ capture with mixed solvents.

6 References

- Gibbins, J., & Lucquiaud, M. (2022). *BAT Review for PCC, V2.0 (including EfW) BAT Review for New-Build and Retrofit Post-Combustion Carbon Dioxide Capture Using Amine-Based Technologies for Power and CHP Plants Fuelled by Gas and Biomass and for Post-Combustion Capture Using Amine-Based and*. <https://ukccsrc.ac.uk/best-available-technology->
- Morken, A. K., Pedersen, S., Nesse, S. O., Flø, N. E., Johnsen, K., Feste, J. K., de Cazenove, T., Faramarzi, L., & Vernstad, K. (2019). CO₂ capture with monoethanolamine: Solvent management and environmental impacts during long term operation at the Technology Centre Mongstad (TCM). *International Journal of Greenhouse Gas Control*, 82(January), 175–183. <https://doi.org/10.1016/j.ijggc.2018.12.018>
- Moser, P., Wiechers, G., Schmidt, S., Veronezi Figueiredo, R., Skylogianni, E., & Garcia Moretz-Sohn Monteiro, J. (2022). Conclusions from 3 Years of Continuous Capture Plant Operation Without Exchange of the Amp/Pz-Based Solvent at Niederaussem – Insights into Solvent Degradation Management. *SSRN Electronic Journal*. <https://doi.org/10.2139/SSRN.4274015>
- Ros, J., Figueiredo, R. V., Srivastava, T., Huizinga, A., Os, P. Van, Wassenaar, H., & Monteiro, J. G. M.-S. (2022). Results of the 2020 and 2021 campaigns of the commercial carbon capture plant at AVR Duiven. *Proceedings of the 16th Greenhouse Gas Control Technologies Conference (GHGT-16)*. <http://dx.doi.org/10.2139/ssrn.4282665>
- V. Figueiredo, R., Srivastava, T., Skaar, T., Warning, N., Gravesteijn, P., van Os, P., Ansaloni, L., Deng, L., Knuutila, H., Monteiro, J., & Goetheer, E. (2021). Impact of dissolved oxygen removal on solvent degradation for post-combustion CO₂ capture. *International Journal of Greenhouse Gas Control*, 112, 103493. <https://doi.org/10.1016/J.IJGGC.2021.103493>

Appendix

Appendix A. Data from liquid sample analysis before and after reclaiming

Component	Unit	Degraded solvent (Rec1)						
		0 hrs	25 hrs	72.5 hrs	146.5 hrs	166 hrs		
Ethanolamine	mg/kg	247970	249727	253310	249221	238862		
Ammonium	mg/kg	1100	991	620	893	1083		
Acetic acid	mg/kg	887.4	952.4	1065.2	1184.4	1217.0		
Formic acid	mg/kg	6039.4	5731.3	5836.0	6095.1	6324.1		
Oxalic acid	mg/kg	2072.6	2120.0	2177.9	2245.3	2305.3		
Nitrate	mg/kg	261.5	252.8	266.8	284.3	303.9		
Nitrite	mg/kg	nd	nd	nd	nd	nd		
CO ₂	mol/l	0.603	0.977	0.960	0.969	1.018		
Water	% w/w	51.3	48.9	47.9	46.2	46.2		
Cr	mg/kg	25.26	26.10	27.55	28.93	29.06		
Cu	mg/kg	1.82	2.43	9.18	26.72	31.32		
Fe	mg/kg	125.28	160.88	174.18	185.52	186.64		
Ni	mg/kg	12.55	12.88	14.21	16.03	16.35		
Zn	mg/kg	8.56	9.55	16.23	31.34	34.92		
Component	Unit	Reclaimed solvent (Rec2)						
		5.5 hrs	24.5 hrs	49 hrs	73.5 hrs	74.5 hrs	99.5 hrs	170 hrs
Ethanolamine	mg/kg	314747	319662	318159	312575	307289	306830	316407
Ammonium	mg/kg	589	413	371	349	556	350	451
Acetic acid	mg/kg	nd	nd	nd	nd	nd	nd	nd
Formic acid	mg/kg	259.4	283.1	310.4	411.2	1006.2	573.9	1040.1
Oxalic acid	mg/kg	27.4	35.9	58.4	90.3	102.7	127.7	202.9
Nitrate	mg/kg	17.7	12.3	13.7	17.6	30.9	23.6	45.7
Nitrite	mg/kg	28.31	9.4	3.91	3.49	15.76	nd	nd
CO ₂	mol/l	1.678	1.674	1.649	1.594	1.547	1.597	1.718
Water	% w/w	60.3	60.2	60.0	60.2	60.2	60.8	58.5
Cr	mg/kg	0.14	0.23	0.31	0.40	0.42	0.51	0.72
Cu	mg/kg	0.73	14.29	35.11	49.03	50.45	65.51	114.92
Fe	mg/kg	1.13	1.57	1.93	2.42	2.44	2.91	3.92
Ni	mg/kg	0.07	0.65	1.42	2.00	2.10	2.75	4.26
Zn	mg/kg	0.27	9.65	23.51	31.95	33.08	41.21	68.14